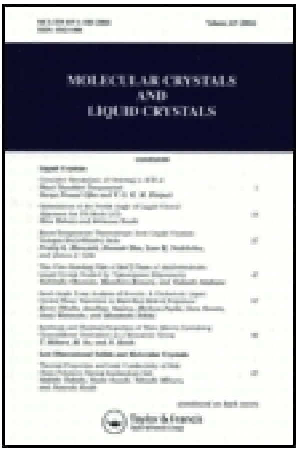

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Generalized Dispersion Model of Orientationally Ordered Phases of Bent-Core Liquid Crystals

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Version of record first published: 30 Jun 2011

To cite this article: L. Longa & G. Pająk (2011): Generalized Dispersion Model of Orientationally Ordered Phases of Bent-Core Liquid Crystals, Molecular Crystals and Liquid Crystals, 541:1, 152/[390]-158/[396]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.570200

Mol. Cryst. Liq. Cryst., Vol. 541: pp. 152/[390]–158/[396], 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.570200

Generalized Dispersion Model of Orientationally Ordered Phases of Bent–Core Liquid Crystals

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Dual symmetry of recently introduced model with quadrupolar and octupolar microscopic interactions [L. Longa, G. Pająk, and T. Wydro, Phys. Rev. E **79***, 040701(R) (2009)] is explored in the mean field approximation. Exemplary phase diagrams with new nematic–like phases are shown. Among them is the homogeneous chiral phase, predicted earlier by Landau theory [T. C. Lubensky, L. Radzihovsky, Phys. Rev. E* **66***, 031704 (2002)].*

Keywords Banana–shaped molecules; chiral phase; duality; molecular theory; octupolar interactions; tetrahedral symmetry

1. Introduction

Banana–shaped molecules are known to form a variety of structures [1], among which are recently observed uniaxial and biaxial nematic phases [2,3], and states of broken chiral symmetry [1]. Using Landau theory Lubensky and Radzihovsky [4] have argued that for a proper understanding of long–range orientational order in these systems the free energy must include polar, quadrupolar and octupolar contributions [4,5]. In our recent paper [6] we initialized a molecular modeling of *V*–shaped systems that follows these ideas. The microscopic modelwe proposed contained quadrupolar and octupolar interactions, referred to common two–fold symmetry axes. The model was shown to stabilize sixspatially homogenous structures.

In this paper we first briefly recall basic properties of this model. Then, we exploreits dual symmetry *i.e.*, a connection between thermodynamical states for oblate and prolate molecules [7,8]. Analysis is summarized with results for exemplary values of molecular interaction coefficients.

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2. The Model

Construction of the Lebwohl–Lasher–type model [9,10] for V–shaped molecules is based on the attractive interaction which is globally invariant with respect to *the full rotation group O(3)*. The interaction potential includes quadrupolar and octupolar contributions, where the latter part contains a term involving the third–rank tensor (**T**) of tetrahedral symmetry. The quadrupolar part comprises, as usual, two second–rank tensors reproducing symmetries of uniaxial ($\mathbf{Q}_U$) and biaxial ($\mathbf{Q}_B$) nematics. The explicit form of the pair potential interaction is given by [6]

$$H_{ij} = -\varepsilon\Big\{\Big(\mathbf{Q}_U(i) + \sqrt{2}\lambda\mathbf{Q}_B(i)\Big)\cdot\Big(\mathbf{Q}_U(j) + \sqrt{2}\lambda\mathbf{Q}_B(j)\Big) + \tau\mathbf{T}(i)\cdot\mathbf{T}(j)\Big\}, \qquad (1)$$

where the scalar product, "·", denotes a full contraction of the Cartesian tensors, and where

$$\mathbf{Q}_U(k) = \sqrt{\frac{3}{2}}\left(\hat{\mathbf{c}}_k \otimes \hat{\mathbf{c}}_k - \frac{1}{3}\mathbf{1}\right), \qquad (2)$$

$$\mathbf{Q}_B(k) = \frac{1}{\sqrt{2}}\left(\hat{\mathbf{a}}_k \otimes \hat{\mathbf{a}}_k - \hat{\mathbf{b}}_k \otimes \hat{\mathbf{b}}_k\right), \qquad (3)$$

$$\mathbf{T}(k) = \frac{1}{\sqrt{6}} \sum_{(\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}})\in\pi(\hat{\mathbf{a}}_k,\hat{\mathbf{b}}_k,\hat{\mathbf{c}}_k)} \hat{\mathbf{x}} \otimes \hat{\mathbf{y}} \otimes \hat{\mathbf{z}}. \qquad (4)$$

The tensors (2–4) are parameterized by the orthonormal tripod $\boldsymbol{\Omega}_k$ of vectors $\left\{\hat{\mathbf{a}}_k, \hat{\mathbf{b}}_k, \hat{\mathbf{c}}_k\right\}$ defining the orientational degrees of freedom of the k–th molecule and by the parity p_k of the tripod: $p_k = \hat{\mathbf{a}}_k \cdot \left(\hat{\mathbf{b}}_k \times \hat{\mathbf{c}}_k\right) = \pm 1$, which is an Ising–type degree of freedom. Summation in (4) is over six permutations of the vectors $\left\{\hat{\mathbf{a}}_k, \hat{\mathbf{b}}_k, \hat{\mathbf{c}}_k\right\}$. Assuming that molecules occupy sites of a three dimensional simple cubic lattice and the interactions are limited to nearest neighbors, the total interaction energy for the system composed of Nsuch molecules is given by

$$H_N = \frac{1}{2}\sum_{\langle i,j\rangle} H_{ij}, \qquad (5)$$

where the summation runs over $i = 1 \ldots N$, and six nearest neighbors j for each i–th molecule. This model for a subsets of coupling constants $\{\varepsilon,\ \lambda,\ \tau\}$ was previously investigated in [6,7].

Equilibrium properties of the system (5) are obtained from the free energy per molecule

$$\frac{F}{N\varepsilon} = -t \lim_{N\to\infty} \frac{1}{N} \ln Z_N, \qquad (6)$$

where $t = k_B T/\varepsilon$ $(\varepsilon > 0)$ is the reduced temperature and

$$Z_N = \underset{(1\ldots N)}{Tr}\left\{\exp\left(-t^{-1}\frac{H_N}{\varepsilon}\right)\right\}. \qquad (7)$$

The *O(3)* invariant measure, denoted Tr in (7), is given by

$$\underset{(1\ldots N)}{Tr} = \prod_{k=1}^{N} \left(\frac{1}{2} \sum_{p_k=\pm 1} \int d\mathbf{\Omega}_k \right). \tag{8}$$

2.1. *Dualsymmetry*

The model (1–8) has an intrinsic symmetry known as duality transformation that relates thermodynamical states of prolate and oblate molecules. The transformation is a direct manifestation of invariance of the partition function (7) with respect to a *global* permutation of molecular axes.

We start with the case of $\tau = 0$, where a simultaneous replacement of $\{\lambda, \mathrm{t}\}$ by

$$\{\lambda', t'\} = \left\{ \frac{\left(\sqrt{\frac{3}{2}} - \lambda\right)}{\left(1 + \sqrt{6}\lambda\right)}, \frac{4t}{\left(1 + \sqrt{6}\lambda\right)^2} \right\} \tag{9}$$

leaves (7) invariant [7,8]. The fixed point, $\lambda^* = 1/\sqrt{6}$, of (9) is known as the self dual point. As the molecular symmetry axis corresponding to the largest absolute eigenvalue of the molecular quad rupole tensor Eq. $\mathbf{Q}_U(i) + \sqrt{2}\lambda\mathbf{Q}_B(i)$, (1), varies with λ (it is the $\hat{\mathbf{c}}_k$-axis for $0 \le \lambda \le 1/\sqrt{6}$ and $\hat{\mathbf{b}}_k$ for $1/\sqrt{6} \le \lambda \le \sqrt{3/2}$), the thermodynamical functions for prolate ($0 \le \lambda \le 1/\sqrt{6}$) ensembles of molecules can be mapped using (9) onto the corresponding functions of their 'dual' oblate ($1/\sqrt{6} \le \lambda \le \sqrt{3/2}$) counter parts, and *vice versa.* An important consequence of this is a possibility of reconstructing the whole phase diagram for $0 \le \lambda \le \sqrt{3/2}$ out of the one known only for $0 \le \lambda \le 1/\sqrt{6}$. Now we extend this property to the case when $\tau \neq 0$.

Tetrahedral interactions are invariant with respect to apermutation of the molecular axes and, hence, the dual symmetry is regained for $\tau \neq 0$, given τ is changed into τ' using the relation

$$\tau' = \frac{4\tau}{\left(1 + \sqrt{6}\lambda\right)^2}, \tag{10}$$

which is identical to that connecting t' and t. As in our previous work [6] we would like to study phase diagrams in the (λ, t) plane. Use of the duality property of the model (1,7) is very helpful here for it allowsto select the minimal sector in the parameter space necessary to reconstruct the complete phase diagrams. But λ dependence of τ, Eq. (10), indicates that the states connected through the duality transformation correspond to different values of τ. For a practical use of (9,10) we need therefore to seek the simplest function $\tau(\lambda)$ fulfilling (10) that can be used tolabel these states. Generally, assuming τ in the original model (1) to depend on λ, the condition (10) can be rewritten in a functional form as

$$\tau'(\lambda) = \tau(\lambda') = \tau\left(\frac{\left(\sqrt{\frac{3}{2}} - \lambda\right)}{\left(1 + \sqrt{6}\lambda\right)} \right) = \frac{4\tau(\lambda)}{\left(1 + \sqrt{6}\lambda\right)^2}. \tag{11}$$

As already pointed out above, $\tau(x) = const$ cannot fulfill (11). The simplest parameterization of the thermodynamic states obeying the relation (11) is the linear one

$$\tau(x) = \frac{1}{2}\left(1 + \sqrt{6}x\right)\,\tau_d, \tag{12}$$

where τ_d is the value of τ at the self dual point: $\tau'\left(1/\sqrt{6}\right) = \tau\left(1/\sqrt{6}\right) \equiv \tau_d$. Hence, the thermodynamically equivalent states $\{\lambda',\ t',\ \tau' = \tau(\lambda')\}$ and $\{\lambda,\ t,\ \tau(\lambda)\}$ in the $(\lambda,\ t)$ plane can be parameterized by the linear relation (12). They are labeled unequivocally by one single parameter τ_d.

2.2. *Mean Field Analysis*

Now we determine exemplary phase diagrams using the mean field approximation and the parameterization (12). In the mean field approximation the free energy F, Eq. (6), should be replaced by F^{MF} given by

$$F^{MF} = -\frac{1}{2}Nd\underset{(1)}{Tr}\left\{P_{eq}(p_1,\mathbf{\Omega}_1)H_{eff}(p_1,\mathbf{\Omega}_1)\right\} - N\beta^{-1}\ln Z_{MF}, \tag{13}$$

where

$$Z_{MF} = \underset{(1)}{Tr}\left\{\exp\left(-\beta dH_{eff}(p_1,\mathbf{\Omega}_1)\right)\right\}, \tag{14}$$

$$H_{eff}(p_1,\mathbf{\Omega}_1) = \underset{(2)}{Tr}\left\{H_{12}P_{eq}(p_2,\mathbf{\Omega}_2)\right\}, \tag{15}$$

$$P_{eq}(p_1,\mathbf{\Omega}_1) = Z_{MF}^{-1}\exp\left(-\beta dH_{eff}(p_1,\mathbf{\Omega}_1)\right). \tag{16}$$

Obtaining phase diagrams requires minimization of (13) with respect to all relevant order parameters entering the stationary, one–particle distribution function (16). In order to identify these order parameters we define real, symmetry–adapted functions, $\Delta^{(L)}_{mn}(\mathbf{\Omega})$, which are linear combination of the Wigner's rotation matrices D^L_{mn} [8]. Then the one–particle distribution function can be expanded in the mean-square convergent series as

$$P(p,\mathbf{\Omega}) = \sum_{l,m,n,s}\frac{2L+1}{8\pi^2}\overline{p_s\Delta^{(L)}_{mn}}p_s\Delta^{(L)}_{mn}(\mathbf{\Omega}), \tag{17}$$

where $p_s = (1,\ p)$, and where the averaged coefficients

$$\overline{X} = \frac{1}{2}\sum_{p=\pm1}\int X(p,\mathbf{\Omega})P(p,\mathbf{\Omega})d\mathbf{\Omega} \equiv Tr\{XP\} \tag{18}$$

are the order parameters. Orthogonality condition for $p_s\Delta^{(L)}_{mn}(\mathbf{\Omega})$, over the $O(3)$ group has the following form:

$$Tr\left\{p_s\Delta^{(L)}_{mn}(\mathbf{\Omega})p_{s'}\Delta^{(L')}_{m'n'}(\mathbf{\Omega})\right\} = \frac{8\pi^2}{2L+1}\delta_{LL'}\delta_{mm'}\delta_{nn'}\delta_{ss'}. \tag{19}$$

Primary order parameters describing symmetry of a given phase, are those which as first become nonzero for given structure *i.e.*, they are defined for the lowest allowed value of L. The upper limit of $L = 3$ covers all relevant order parameters for the investigated model: a) $\overline{\Delta_{00}^{(2)}}$ and $\overline{\Delta_{02}^{(2)}}$ for uniaxial nematic phase; b) additionally $\overline{\Delta_{22}^{(2)}}$ and $\overline{\Delta_{20}^{(2)}}$ for biaxial nematic phase; c) only $\overline{\Delta_{22}^{(3)}}$ for tetrahedral phase (for detailed analysis of this symmetry, see publication [11]); d) $\overline{p\Delta_{20}^{(2)}}$ and $\overline{p\Delta_{22}^{(2)}}$ along with uniaxial and tetrahedral order parameters for uniaxially distorted tetrahedral phase of D_{2d} symmetry; e) for chiral structure all above mentioned order parameters are nonzero in addition to $\bar{p}$, $\overline{p\Delta_{02}^{(2)}}$ and $\overline{p\Delta_{00}^{(2)}}$. For $L \leq 3$ the explicit form of $\Delta_{mn}^{(L)}$ is

$$\Delta_{mn}^{(L)} = \left(\frac{1}{\sqrt{2}}\right)^{2+\delta_{m0}+\delta_{n0}} \left(\mathcal{D}_{mn}^{L} + (-1)^{L}\mathcal{D}_{m-n}^{L} + (-1)^{L}\mathcal{D}_{-mn}^{L} + \mathcal{D}_{-m-n}^{L}\right). \tag{20}$$

Utilizing properties of the functions (20) we can rewrite the mean field Hamiltonian (15) and hence also the Eqs. (13–17) in terms of $\Delta_{mn}^{(L)}$. In particular H_{eff} reads

$$\begin{aligned} H_{eff} = & -\varepsilon\left(\overline{\Delta_{00}^{(2)}} + \sqrt{2}\lambda\overline{\Delta_{02}^{(2)}}\right)\left(\Delta_{00}^{(2)}(\mathbf{\Omega}) + \sqrt{2}\lambda\Delta_{02}^{(2)}(\mathbf{\Omega})\right) - \varepsilon\tau\overline{\Delta_{22}^{(3)}}\Delta_{22}^{(3)}(\mathbf{\Omega}) \\ & - \varepsilon\left(\overline{\Delta_{20}^{(2)}} + \sqrt{2}\lambda\overline{\Delta_{22}^{(2)}}\right)\left(\Delta_{20}^{(2)}(\mathbf{\Omega}) + \sqrt{2}\lambda\Delta_{22}^{(2)}(\mathbf{\Omega})\right) \equiv \varepsilon V_{eff}. \end{aligned} \tag{21}$$

The self consistent Eq. (16) for the one–particle distribution function becomes now reduced to a system of five nonlinear equations for the order parameters

$$\overline{\Delta_{mn}^{(L)}} = Z_{MF}^{-1} \underset{(1)}{Tr}\left\{\Delta_{mn}^{(L)}(\mathbf{\Omega}_1)\exp\left(-dt^{-1}V_{eff}(p_1, \mathbf{\Omega}_1)\right)\right\}, \tag{22}$$

which can be solved numerically.

3. Results and Discussion

Phase diagrams for the model (1,13), with the tetrahedral coupling constant in the interaction potential (1) being replaced by the relation (12), are obtained for fixed values of τ_d. They are presented in the (λ, t) plane, where $t = (\beta\varepsilon(1 + 2\lambda^2))^{-1}$ is the renormalized reduced temperature. Exemplary phase diagrams are shown in Figures 1, 2 with the parameters chosen such that the high–temperature region is dominated by either tetrahedral phase or standard nematic phases.

The first case, illustrated in Figure 1, occurs when tetrahedral structure (T) prevails ($\tau_d \geq 3.08$). At low temperatures only highly–symmetric phases are stabilized, which are uniaxially distorted tetrahedral phases denoted as prolate (N_{T+}) and oblate (N_{T-}), and a chiral phase (N_T^*) of D_2 symmetry. These phases are homogenous, orientationally ordered nematic–like structures. For $\tau_d < 28/15$ a new class of the diagrams, like the one shown in Figure 2, emerges. Here, at low temperatures the same structures occur as in Figure 1, but the transitions leading to them go through conventional uniaxial (N_U) and biaxial (N_B) nematic phases.

Summarizing, theanalysis of the model (1) with inclusion of the duality relation reveals the same stable structures as reported earlier in [6]. However, the analysis is less time–consuming for the sector of relevant parameters is minimal. In the new

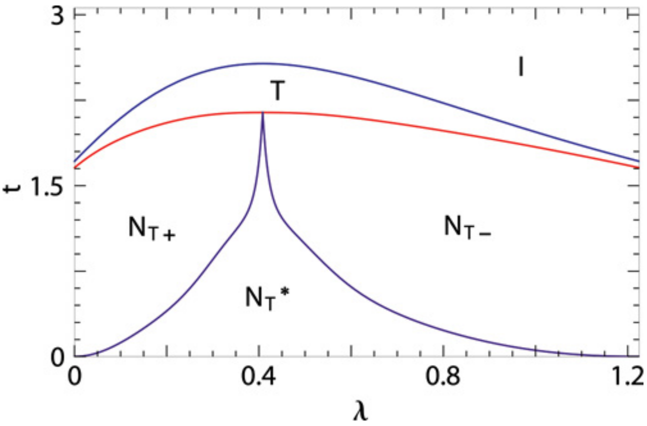

Figure 1. Mean field phase diagram for $\tau_d = 4$. Blue line represents phase transitions from isotropic structure to tetrahedral phase. Red and violet lines reflect the transitions to the N_T and N_T^* phases respectively.

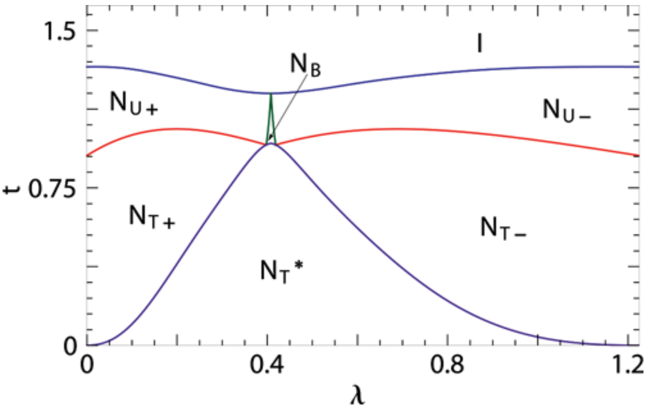

Figure 2. Mean field phase diagram for $\tau_d = 1$. Blue line represents phase transitions from isotropic structure to the conventional nematics. The green line shows transitions to the biaxial phase (for the remaining colors, see captions to Figure 1).

parameterization the obtained phase diagrams are also more symmetricas we make use of the duality property of the original model. The mechanism responsible for stabilization of the phases has already been reported in [6]. We recall that all highly–symmetric phases of the model are stabilized as a result of an interplay between quadrupolar and octupolar interactions, and where tetrahedral order is indispensable. In particular, the stabilization of the chiral phase requires condensation of biaxial and tetrahedral order parameters simultaneously.

Acknowledgment

The work has been supported by the International PhD Projects Programme of the Foundation for Polish Science within the European Regional Development Fund of the European Union, agreement no. MPD/2009/6.

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